



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : F21K 2/08	A1	(11) International Publication Number: WO 00/29779 (43) International Publication Date: 25 May 2000 (25.05.00)
(21) International Application Number: PCT/US99/27024 (22) International Filing Date: 16 November 1999 (16.11.99) (30) Priority Data: 60/108,783 17 November 1998 (17.11.98) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 60/108,783 (CIP) Filed on 17 November 1998 (17.11.98) (71) Applicant (for all designated States except US): REGENTS OF THE UNIVERSITY OF CALIFORNIA [US/US]; 5th Floor, 1111 Franklin Street, Oakland, CA 94607-5200 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): YANG, Yang [—/US]; 13730 Bayliss Road, Los Angeles, CA 90049 (US). CHANG, Shun-Chi [—/US]; 1645 Federal Avenue #3, Los Angeles, CA 90025 (US). (74) Agents: RITTMASER, Ted, R. et al.; Foley & Lardner, Suite 500, 3000 K Street, N.W., Washington, D.C. 20007-5109 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PROCESS FOR GENERATING LUMINESCENCE EMISSIONS FROM POLYMER SOLUTIONS, GELS, AND LIQUID POLYMERS IN A COMPACT CELL CONFIGURATION, AND DEVICE EMPLOYING SAME <div style="text-align: center;"> </div>		
(57) Abstract <p>A semiconductor device for producing an indicator in response to a stimulus is disclosed. The semiconductor device includes two electrodes, each electrode affixed to a separate substrate. A polymer solution layer is sandwiched between the two electrodes. When a voltage is applied across the two electrodes, current flows between the two electrodes and through the polymer solution layer, which produces luminescence. Pure polymer solutions or gels, polymer solution/organic dye blends, and small organic molecules may be used to produce luminescence at a particular color and brightness.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

5 PROCESS FOR GENERATING LUMINESCENCE EMISSIONS
FROM POLYMER SOLUTIONS, GELS, AND LIQUID POLYMERS
IN A COMPACT CELL CONFIGURATION, AND DEVICE
EMPLOYING SAME

Cross-Reference to Related Applications

10 Embodiments of the present invention relate to Provisional Application Serial No. 60/108,783, filed November 17, 1998. The contents of this application are incorporated by reference herein.

Background of the Invention

1. Field of the Invention

15 The present invention relates, generally, to polymer electro-generated luminescent devices, and in particular embodiments, to methods for generating luminescence emissions from conjugated polymer solutions, gels, and liquids in a compact cell configuration, and devices employing the same.

2. Description of Related Art

20 Inorganic semiconductors, such as silicon and gallium arsenate, are often used to produce modern semiconducting and photonic devices. The processing of these inorganic semiconductor devices can be complicated and costly, and typically includes process steps such as the growing of crystals, the slicing and polishing of wafers, and building of integrated electronic circuits on the wafer. By comparison, conventional polymers
25 (sometimes referred to as plastics) are relative easy to process. For example, the fabrication of traditional plastic parts may include relatively simple process steps such as the injection of molten plastic material into molds. Polymers are also flexible, lightweight, and can be fabricated over large surface areas. However, conventional plastics are not semiconducting, and are therefore unsuitable for the fabrication of semiconductor devices.

Conjugated polymer is an organic material that combines the electrical and optical properties of semiconductors and the processability of conventional plastics. The semiconducting properties of conjugated polymers originate from the delocalized pi orbitals formed in carbon containing compounds, such as poly(phenylenevinylene), polythiophene (PT), and poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV). Unlike conventional polymers, conjugated polymers contain double bonds which make the material semiconducting rather than insulating. Conjugated polymers retain the low-cost processing benefits, flexibility, light weight, and large-scale producibility of conventional polymers and the general semiconducting characteristics of silicon.

Conjugated polymer devices are typically solid-state devices fabricated by spin-coating. A typical polymer LED consists of a thin film of a luminescent conjugated polymer sandwiched between an anode and a cathode, on top of a transparent glass substrate. Indium tin-oxide (ITO) is most frequently used as the anode. It has the desirable properties of being conductive with a relatively high work function, and optically transparent. Calcium (work function $\phi = 2.9\text{eV}$), aluminum ($\phi = 4.3\text{eV}$), or magnesium/silver alloy ($\phi = 3.7\text{eV}$) are often used as the cathode. On the application of a suitable bias, electrons and holes are injected from the cathode and the anode respectively into the polymer. Some of the injected carriers subsequently undergo radiative recombination within the polymer thin film with the resulting release of energy in the form of an electroluminescence emission.

Another class of organic semiconducting materials is the class of conjugated small organic molecules. Conjugated organic compounds (organics) are defined herein to include polymers and small organic molecules (organics comprised of single molecules). Small organic molecules share similar physical (electronic and optical) properties with conjugated polymers, but utilize somewhat different processing techniques. Organic molecules are usually processed using thermal sublimation at ultra high vacuum environments to form desired thin films, with a typical thickness of about 100 nm. Organic molecules often use device structures similar to those used with conjugated polymers, i.e. organic thin films sandwiched between two electrodes. Solid-state small molecular organic LEDs (OLEDs) have been commercialized by Pioneer in automobile audio systems.

In addition to solid state organic and polymer devices, another class of device utilizes organic dye solution as the luminescence active medium. There are two formats of

such devices known in the art: the closed-cell and circulated-cell configurations. The active media were organic dye molecules dissolved in organic solvents, and it has been demonstrated that electrogenerated chemiluminescence (ECL) was responsible for the generation of the light. Others skilled in the art have reported the observation of
5 electrically pumped laser action from a circulation cell employing an organic dye solution inside a resonant cavity. However, the disadvantage of using organic dye solution is the self-quench effect caused by high concentrations of dye solutions. It has been observed that most organic dyes have high photoluminescence efficiency when the concentration of dye solution is low. However, when the concentration is high, the photoluminescence (PL)
10 efficiency decreases dramatically, and the PL efficiency is nearly zero when the dye is in a solid format. Due to polymer conformation, this PL quench effect is not as significant in the conjugated polymers as in the organic dyes. Hence, one is able to apply a very high concentration of polymer solutions or polymer gels to the polymer solution device. The high concentration solutions and gels have several advantages, including: (1) the ability to
15 carry a much higher current density, thus achieving a much brighter device, and (2) overlap polymer chains for achieving higher carrier mobility. In addition, different functional side groups could be attached to the polymer structure for achieving desired physical, electrochemical, and other effects.

Summary of the Disclosure

20 Therefore, it is an advantage of embodiments of the present invention to provide a device and method for generating luminescence emissions from conjugated polymer solutions, gels, and liquids (polymer liquid or liquid is defined as polymers with a low melting point that is liquid at room temperature and therefore does not require an organic solvent) in a compact cell configuration (which covers circulating or closed cells) that is
25 simple, low cost, and time-efficient.

It is a further advantage of embodiments of the present invention to provide a device and method for generating luminescence emissions from conjugated polymer solutions in a compact cell configuration that has higher intrinsic fluorescence efficiency and higher quantum efficiency than solid polymer material, which results in power savings.

30 It is a further advantage of embodiments of the present invention to provide a device and method for generating luminescence emissions from polymer solutions in a compact

cell configuration that is self-illuminating as compared to liquid crystal displays (LCDs), and whose fabrication process is similar enough to that of LCDs that manufacturing facilities currently making LCDs can easily be converted into state-of-the-art polymer solution LED (SLED), gel LED (GLED) and liquid LED (LLED) manufacturing facilities.

5 It is a further advantage of embodiments of the present invention to provide a device and method for generating luminescence emissions from polymer solutions, gels, and liquids in a compact cell configuration over a large area with high reliability and reduced likelihood of pin-hole formation.

10 It is a further advantage of embodiments of the present invention to provide a device and method for generating luminescence emissions from polymer solutions, gels, and liquids in a compact cell configuration within a self-encapsulated device that does not require a capping layer and that can be edge-sealed by the drying of excess polymer solution.

15 It is a further advantage of embodiments of the present invention to provide a device and method for generating luminescence emissions from polymer solutions in a compact cell configuration within a transparent device that can be vertically stacked to achieve multi-color displays with high resolution.

20 These and other advantages are accomplished according to a semiconductor device for producing an indicator in response to a stimulus. The semiconductor device includes two electrodes, each electrode affixed to a separate substrate. A layer of polymer solution, gel or liquid is sandwiched between the two electrodes. When a voltage is applied across the two electrodes, current flows between the two electrodes and through the polymer solution layer, which produces luminescence. Pure polymer solutions, gels, or liquids, polymer solution/organic dye blends, and small organic molecules may be used to produce
25 luminescence at a particular color and brightness.

These and other objects, features, and advantages of embodiments of the invention will be apparent to those skilled in the art from the following detailed description of embodiments of the invention, when read with the drawings and appended claims.

Brief Description of the Drawings

30 FIG. 1 is a side view of a closed SLED structure according to an embodiment of the present invention.

FIG. 2 is a graph illustrating the absorption, photoluminescence, and emission spectra of SLED using MEH-PPV solution as the active material according to an embodiment of the present invention.

5 FIG. 3 is a graph illustrating the absorption, photoluminescence, and emission spectra of SLED using BDOH-PF solution as the active material according to an embodiment of the present invention.

FIG. 4 is a graph illustrating the current-brightness-voltage curves for the SLED using MEH-PPV solution as the active material according to an embodiment of the present invention.

10 FIG. 5 is a graph illustrating the current-brightness-voltage curves for the SLED using BDOH-PF solution as the active material according to an embodiment of the present invention.

FIG. 6 is a graph illustrating the semi-log plot of the I-L-V curves of a GLED according to an embodiment of the present invention.

15 FIG. 7 is a graph illustrating the semi-log plot of the I-L-V curves of a GLED with the addition of salt according to an embodiment of the present invention.

FIG. 8 is a graph illustrating the current-brightness-voltage curves for the SLED using MEH-PPV:DCM solution as the active material according to an embodiment of the present invention.

20 FIG. 9 is a graph illustrating the current-brightness-voltage curves for the SLED using BDOH-PF:DCM solution as the active material according to an embodiment of the present invention.

FIG. 10 is a graph illustrating the semi-log plot of the I-L-V curves of a SLED blend with liquid crystals according to an embodiment of the present invention.

25 FIG. 11 is a graph illustrating the I-V-L curves of SLEDs using BDOH-PF as the active medium with and without buffer layers according to an embodiment of the present invention.

FIG. 12 is a side view of a vertically stacked transparent SLED according to an embodiment of the present invention.

30 FIG. 13 is an exploded perspective and side view diagram of one possible method to construct a multicolor display from SLEDs wherein the partition of multicolor SLEDs is

achieved through the patterning of photoresist or other means according to an embodiment of the present invention.

FIG. 14 is a side view diagram of the SLED of FIG. 13 according to an embodiment of the present invention.

5

Detailed Description of Preferred Embodiments

In the following description of preferred embodiments, reference is made to the accompanying drawings which form a part hereof, and in which is shown by way of illustration specific embodiments in which the invention may be practiced. It is to be understood that other embodiments may be utilized and structural changes may be made without departing from the scope of the preferred embodiments of the present invention.

Conjugated polymer is an organic material that combines the electrical and optical properties of semiconductors and the processability of conventional plastics. Conjugated polymers retain the low-cost processing benefits, flexibility, light weight, and large-scale producibility of conventional polymers and the general semiconducting characteristics of silicon. For purposes of the following description, references to polymer should be understood to mean conjugated polymer.

In embodiments of the present invention, luminescence emission is generated from polymer solutions in a compact polymer solution cell configuration. FIG. 1 illustrates a polymer solution light-emitting device (SLED) 10 comprising a thin layer of a polymer solution or gel 12 sandwiched between two indium tin oxide (ITO)/glass substrates 14 in a closed-cell configuration with the thickness of the solution layer ranging from 1 to 2 μm according to a preferred embodiment. It should be noted that although not illustrated in FIG. 1, in alternative embodiments GLEDs and LLEDs may be fabricated with a similar structure. In addition to the closed cell, a circulating cell may be realized by attaching a reservoir to the cell, the solution reservoir having two tubes, one which acts as an inlet for the solution and another which acts as an outlet.

When biased, the device 10 turns-on near the bandgap energy and emits luminescence 16. The luminescence emission spectra are consistent with the photoluminescence spectra obtained from the polymer solution 12, and are a product of the electrochemiluminescence effect. In alternative embodiments, SLEDs 10 can be fabricated

as transparent emissive devices when both electrodes 18 and substrates 14 are transparent materials.

The emitting efficiency of a light-emitting device is proportional to its intrinsic fluorescence efficiency. Polymer solutions 12 have higher intrinsic fluorescence efficiency than solid polymer material. In addition, polymer solutions 12 can yield higher quantum efficiency (the number of electrons converted into photons) than solid polymer material. The improvement in efficiency realized by SLEDs 10 translates into power savings, an advantage especially important for portable devices such as laptop computers. Also, portable devices often use liquid crystal displays (LCDs), which require a lamp for illumination. Because SLEDs 10 are self-illuminating, no lamps are required. Furthermore, because the fabrication of LCDs, which comprise liquid crystal material sandwiched by two electrodes attached to glass plates, is so similar to SLED fabrication, manufacturing facilities that currently make LCDs can easily be converted into state-of-the-art SLED manufacturing facilities.

In preferred embodiments of the present invention, the polymer solution preparation process is performed in a nitrogen environment. In preferred embodiments, polymer solutions 12 such as poly(phenylene vinylene) (PPV) derivatives or polyfluorene (PF) derivatives may be employed. One PPV derivative that may be used in an alternative embodiment is poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV), and one polyfluorene derivative that may be used in an alternative embodiment is poly[9,9-bis(3,6-dioxahexyl)-fluorene-2,7-diyl] (BDOH-PF), prepared in concentrations ranging from 0.1 wt % to 20 wt %.

The molecular weight of the polymers described above covers a range from less than 10,000 to higher than 1 million. It should be noted, however, that other luminescent nanocrystals, oligomers (polymer with small repeat units), and conjugated polymers and their blends also fall within the scope of the present invention. The solvents used to dissolve these polymers are cyclohexanone, dichloro-benzene, and xylene; however, other organic solvents are also possible. In addition to the solution format, it is also possible to process the polymers into gel formats (polymer gel is a high concentration polymer solution such that the polymer forms an interpenetrated network) or liquid polymer formats (polymer with a low melting point that is liquid at room temperature and therefore does not require an organic solvent) for the polymer SLED 10.

For purposes of example and illustration only, FIGs. 2 and 3 are graphs of the absorption (Abs) 20, photoluminescent (PL) 22, and electroluminescent (EL) 24 spectra for a typical SLED 10 made of MEH-PPV and BDOH-PF solutions 12, respectively, according to embodiments of the present invention. For purposes of example and illustration only, FIGs. 4 and 5 are graphs of the current-voltage (I-V) curve 34 and light-voltage (L-V) curve 36 for a typical SLED 10 made of MEH-PPV and BDOH-PF solutions 12, respectively, according to embodiments of the present invention. The I-V curves indicate that significant charge injection occurs around 2 volts (see reference character 26) and 3.5 volts (see reference character 28) for MEH-PPV and BDOH-PF respectively, which is consistent with the bandgap energy of these two polymers. The bandgap energy is taken as the measured energy of the edge of the absorption spectra, which is consistent with the values obtained from the difference of oxidation and reduction potentials of these materials. However, the voltage for the onset of photon emission is around 3 volts (see reference character 30) and 6 volts (see reference character 32) for MEH-PPV and BDOH-PF respectively, which is higher than that required for the injection of electrical current.

FIG. 6 is a graph illustrating the semi-log plot of the I-L-V curves of a GLED according to an embodiment of the present invention. It should be noted in FIG. 6 that current saturates at voltages higher than 6 volts (see reference character 50). For purposes of comparison, FIG. 7 is a graph illustrating the semi-log plot of the I-L-V curves of a GLED with the addition of a very small amount of salt according to an embodiment of the present invention. A comparison of FIGs. 6 and 7 demonstrates that the addition of salt significantly enhanced charge injection at low voltages. However, current still saturates at voltages higher than 3 volts (see reference character 52).

The operating mechanism of the SLED 10 is due to electrogenerated chemiluminescence (ECL). For BDOH-PF, the onset of charge injection in the SLED 10 at 3.5 volts is indicative of the initiation of the oxidation and reduction process of BDOH-PF. ECL involves the movement of the electrically charged molecules under the influence of the applied electrical field. When biased, some of the molecules are oxidized near the anode side and some of them are reduced near the cathode side. Under the influence of the applied electric field, the oxidized molecules migrate toward the cathode while the reduced molecules migrate toward the anode. The photons are generated by the radiative recombination of the encountering oppositely charged molecules. Although the conjugated

polymers used in SLEDs 10 have a high molecular weight, the motion of the molecules is not significantly hindered. However, the delay of photon emission observed in the L-V curve is due to the higher field required to enable the migration of the charged polymer from one electrode to the other.

5 In addition to the pure polymer solutions 12 described above, in alternative embodiments the polymer solution 12 may be blended with other polymers such as, but not limited to, liquid crystal compounds, or organic dye (DCM) which may either change the emission color of the device or enhance the charge injection and transport capability. For purposes of example and illustration only, the I-V curve 38 and L-V curve 40 of the
10 SLEDs 10 using solutions of MEH-PPV:DCM and BDOH-PF:DCM are shown in FIGs. 8 and 9 according to embodiments of the present invention. The concentration of dye may be adjusted to obtain the highest device performance. In further alternative embodiments, the polymer solution 12 may comprise small organic molecules such as Almq3 (tris(4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran) at concentrations of 1 %
15 to 20% to enhance the device performance. FIG. 10 illustrates the I-V curve (see reference character 58) and L-V curve (see reference character 60) of MEH-PPV blended with liquid crystal (LC) according to an embodiment of the present invention.

In other alternative embodiments of the present invention, a (porous) buffer polymer or organic layer is pre-coated onto at least one of the ITO electrodes, and the
20 polymer solution 12 is then diffused into this buffer layer. A buffer polymer or organic layer, as defined herein, is a layer coated on the surface of the electrode which prevent the electrode from reacting (chemically or electrochemically) with polymer solutions, gels, and liquids. In addition, this buffer layer might enhance the charge injection. The advantage of using a buffer layer is to stabilize the polymer solution 12 and prevent it from
25 vaporizing, while preserving the high mobility of polymer molecules. FIG. 11 shows the comparison of two SLEDs (devices A and B) with and without buffer layers according to embodiments of the present invention. FIG. 11 is a graph illustrating the I-V-L curves of SLEDs using BDOH-PF as the active medium. Device A (see reference character 54) utilized ITO/PEDOT and ITO/Alq3 bilayer electrodes as the anode and the cathode.
30 Device B (see reference character 56) utilized Pure ITO electrodes as the anode and the cathode.

In preferred embodiments, the fabrication of SLEDs is performed in a nitrogen environment. Electrode material is first deposited onto a glass substrate via a proper method such as sputtering or thermal evaporation. In alternative embodiments, the electrode materials may comprise ITO, gold, and aluminum. However, it should be noted
5 that the use of other metals, conductive oxide, or conducting polymers as electrode material also fall within the scope of embodiments of the present invention. The ITO/glass substrates are baked at high temperature (100°C in a preferred embodiment) for several hours before they are used.

In preferred embodiments, the ITO/glass substrates are then pre-sealed using epoxy,
10 forming an empty void or cell between the ITO/glass substrates. By creating a vacuum within the empty cell, the polymer solution is then forced into the cell by air pressure from the atmosphere. A similar approach may be adopted to fabricate SLEDs, GLEDs, and LLEDs.

In alternative embodiments, several drops of polymer solution are deposited on top
15 of a pre-cleaned ITO/glass substrate. The thickness of the polymer solution layer is controlled by embedding glass beads, ranging from 1- 2 μm , within the polymer solution. However, in alternative embodiments, other spacing devices or protrusions formed in one or both of the electrodes may also be used to achieve the requisite spacing. Another pre-cleaned ITO/glass or Al/glass substrate is then placed on top of the first ITO/glass substrate
20 with the two electrodes facing each other, with the polymer solution situated between the two substrates. These two substrates are pushed against each other by the application of an external force, resulting in the simultaneous ejection of the extra polymer solution from the sides of the SLED. On drying, this extra polymer solution forms a seal, which prevents solvent vaporization from the sandwich structure.

The SLED processing described above is advantageous in its simplicity, its large
25 area processing capability, and its pin-hole free nature. The SLED is also a self-encapsulated device since it does not require a capping layer; the top ITO/glass plate serves as the device capping layer. Furthermore, due to the use of dual ITO/glass substrates, the SLED can be a highly transparent device. In alternative embodiments of the present
30 invention illustrated in FIG. 12, a multi-color display 42 comprised of three vertically stacked, transparent, red-green-blue SLEDs 10 with high-contrast can be achieved within a

small surface area without the need for separate horizontally arranged red, green, and blue LEDs.

In addition to the multi-color display 42 comprised of three vertically stacked red, green, and blue SLEDs 10 described in FIG. 12 above, in alternative embodiments of the present invention illustrated in FIG. 13, a SLED multicolor display 44 can also be achieved through traditional two dimensional red-green-blue pattern of individual pixels. Due to the flow characteristics of the polymer solution 12, it is necessary to confine the polymer solution 12 within a closed cell. In preferred embodiments, this confining is achieved through a patterned polymer (or other material) partition mask 46. In alternative
5 10 15 20
embodiments, this partition mask can be fabricated using photolithographic technology, a stamping technique, or the like. In preferred embodiments, the polymer (or other organic and inorganic compound) solutions 12 can be deposited using inkjet printing. Column anodes 62 oriented in one direction are attached to a glass substrate (not shown in FIG. 13), and ITO row electrodes 48 oriented in another direction are also attached to a glass substrate 14. The column anodes 62 and ITO row electrodes 48 sandwich the partition mask 46 containing the red, green, and blue polymer solutions 12. By applying a voltage across a particular column anode 62 and ITO row electrode 48, the SLED at the intersection of the FIG. 14 column anode 62 and ITO row electrode 48 will produce luminescence. This type of display is known as a passive matrix display. FIG. 14 illustrates a side view of the SLED multicolor display 44 and the sandwiching effect of the column anodes 62 and ITO row electrodes 48 about the red, green, and blue color polymer solutions 12 according to an embodiment of the present invention.

In addition to the passive matrix display described above, an active matrix driving scheme using transistors can be applied to displays made of SLEDs, GLEDs, and LLEDs.
25 30
A transistor is a three terminal device consisting of a source, a drain, and a gate. In an active matrix display, the gate and source electrodes of thin film transistors or regular transistors are fabricated in a matrix on a first substrate. A second substrate is then placed in proximity to the first substrate. An electrode fabricated on the second substrate behaves as the drain electrode. A polymer solution layer is then sandwiched between the source and drain and the light-emitting device is switched on and off by the gate electrode. The advantage of using transistors to drive the display panel is that it does not require the fundamental light-emitting element to possess diode behavior.

Embodiments of the present invention can be applied to a wide variety of devices and systems. Examples include, but are not limited to, using SLEDs to form solid or flexible light sources for different environments such as the surface of a watch, or integrating SLEDs into the top surface of a reflective liquid crystal display for use as the illuminating light source. SLEDs can also be used to create a "smart window" which is transparent in bright light, but becomes a light source in low light. SLEDs can also form emissive displays, either monochrome or multicolor, when pixelated into multiple individual pixels. In addition to light-emitting devices, SLEDs can also be used as electronic devices. Examples include, but are not limited to, transistors, photo sensors, and x-ray sensors.

Therefore, embodiments of the present invention provide a device and method for generating luminescence emissions from polymer solutions, gels, and liquids in a compact cell configuration that is simple, low cost, and time-efficient. Polymer solutions according to embodiments of the present invention have a higher intrinsic fluorescence efficiency and higher quantum efficiency than solid polymer material, which results in power savings. Polymer solutions can be applied into SLEDs over a large area with high reliability and reduced likelihood of pin-hole formation. Furthermore, SLEDs can be fabricated as self-encapsulated devices that do not require a capping layer capable of being edge-sealed by the drying of excess polymer solution.

SLEDs according to embodiments of the present invention can be fabricated as transparent devices that can be vertically stacked to produce reduced surface area multi-color displays and high resolution display devices. SLEDs also afford several advantages over conventional LCDs. SLEDs are self-illuminating as compared to liquid crystal displays (LCDs), and the fabrication process of SLEDs is similar enough to that of LCDs that manufacturing facilities currently making LCDs can easily be converted into state-of-the-art SLED manufacturing facilities.

What is claimed is:

1. A semiconductor device for producing an indicator in response to a stimulus, the semiconductor device comprising:
 - 5 a substrate for supporting the semiconductor device;
 - at least one first electrode supported by the substrate;
 - at least one second electrode supported by the substrate for introducing current flow between the at least one first electrode and the at least one second electrode;
 - and
 - 10 at least one polymer solution layer supported between the at least one first electrode and the at least one second electrode for generating an indicator produced by the semiconductor device in response to the stimulus.
2. A device as recited in claim 1, the at least one polymer solution layer comprising semiconducting material for encouraging current flow between the at least one
15 first electrode and the at least one second electrode in response to the stimulus of a voltage applied across the at least one first electrode and the at least one second electrode.
3. A device as recited in claim 2, the at least one polymer solution layer comprising poly (phenylene vinylene) (PPV) derivatives prepared in concentrations ranging from approximately 0.1 wt % to approximately 20 wt %.
- 20 4. A device as recited in claim 2, the at least one polymer solution layer comprising polyfluorene (PF) derivatives prepared in concentrations ranging from approximately 0.1 wt % to approximately 20 wt %.
5. A device as recited in claim 2, the at least one polymer solution layer comprising a blend of polymer solutions.
- 25 6. A device as recited in claim 5, one polymer solution in the blend of polymer solutions comprising a liquid crystal compound.

7. A device as recited in claim 2, the at least one polymer solution layer comprising a blend of polymer solution and organic molecules.
8. A device as recited in claim 2, the at least one polymer solution layer comprising a polymer gel.
- 5 9. A device as recited in claim 2, the at least one polymer solution layer comprising nanocrystals.
- 10 10. A device as recited in claim 2, the at least one polymer solution layer comprising a liquid polymer.
11. A device as recited in claim 2, further including at least one buffer layer of organic compounds, each buffer layer supported by one of the at least one first electrode and the at least one second electrode, the at least one polymer solution layer comprising polymer solution diffused into the buffer layer for stabilizing the polymer solution layer and preventing vaporization of the polymer solution layer.
- 15 12. A device as recited in claim 1, the at least one first electrode and the at least one second electrode comprising indium tin-oxide.
- 20 13. A device as recited in claim 2, the substrate, the at least one first electrode, and the at least one second electrode comprising a transparent material, the device comprising a plurality of polymer solution layers in a vertical stack, each polymer solution layer supported between a corresponding first electrode and second electrode and comprising a material capable of producing luminescence at a particular color.
14. A device as recited in claim 2, the device comprising a plurality of polymer solution layers in a horizontal array, each polymer solution layer supported between a corresponding first electrode and second electrode and comprising a material capable of producing luminescence at a particular color.

15. A process for fabricating a semiconductor device capable of producing an indicator in response to a stimulus, the process comprising the steps of:

supporting at least one first electrode over a substrate;

supporting at least one polymer solution layer above each first electrode such

5 that one polymer solution layer is in contact with each first electrode; and

supporting at least one second electrode over each polymer solution layer.

16. A process as recited in claim 15, further including the steps of:

pre-sealing edges of at least one pair of first electrodes and second electrodes to form an empty cell between the first electrode and second electrode;

10 creating a vacuum within the empty cell; and

forcing polymer solution into the empty cell by external air pressure.

17. A process as recited in claim 15, further including the steps of:

supporting at least one buffer polymer layer on one of the at least one first electrode and the at least one second electrode; and

15 diffusing polymer solution into the buffer polymer layer for stabilizing the polymer solution layer and preventing vaporization of the polymer solution layer and preventing chemical and electrochemical reactions at the at least one first electrode and the at least one second electrode.

18. A process as recited in claim 15, further including the steps of:
supporting at least one transparent first electrode over a transparent substrate
and supporting at least one transparent second electrode over each polymer solution layer;
and
5 supporting a plurality of polymer solution layers in a vertical stack, each
polymer solution layer supported between a corresponding first electrode and second
electrode and comprising a material capable of producing luminescence at a particular
color.
19. A process as recited in claim 15, the process further including the steps of:
10 confining a plurality of polymer solution layers within closed cells using a
partition mask;
arranging the closed cells in a two-dimensional array;
orienting the at least one first electrode in a first direction and orienting the
at least one second electrode in a second direction, the first and second directions being in
15 alignment with the two-dimensional array such that each polymer solution layer is
supported between a corresponding first electrode and second electrode.
20. A process as recited in claim 19, the process further including the steps of:
incorporating transistors into the device by supporting a third electrode
within each closed cell in the two-dimensional array for controlling current flow between
20 the first electrode and second electrode corresponding to each closed cell.

21. An emissive system for presenting visual images, the emissive system comprising:

a substrate for supporting the emissive system;

at least one first electrode supported by the substrate;

5 at least one second electrode supported by the substrate for introducing a current flow between the at least one first electrode and the at least one second electrode;

at least one polymer solution layer supported between the at least one first electrode and the at least one second electrode for generating an indicator when a voltage stimulus is applied across the first electrode and the second electrode; and

10 a voltage source for selectively applying the voltage stimulus across the at least one first electrode and the at least one second electrode.

22. A system as recited in claim 21, the substrate, the at least one first electrode, and the at least one second electrode comprising a transparent material, the system comprising a regular array of light-emitting devices, each light-emitting device comprising
15 three vertically stacked polymer solution layers supported between a corresponding first electrode and second electrode comprised of material capable of producing red, green, and blue luminescence, the regular array forming a multi-color light-emitting display when current flows through the polymer solution layers.

23. A system as recited in claim 21, the system comprising a plurality of
20 polymer solution layers in a regular array of groups, each group comprising three horizontally arranged polymer solution layers comprised of material capable of producing red, green, and blue luminescence, the regular array forming a multi-color light-emitting display when current flows through the polymer solution layers.

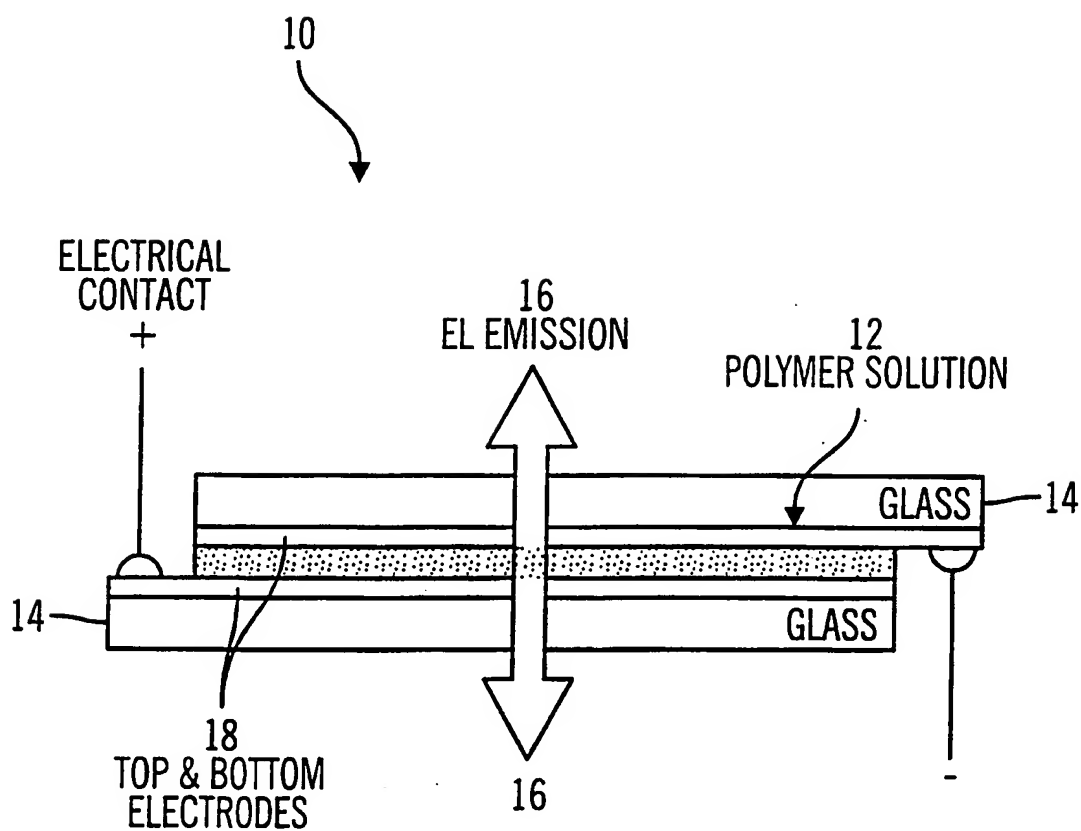


FIG. 1

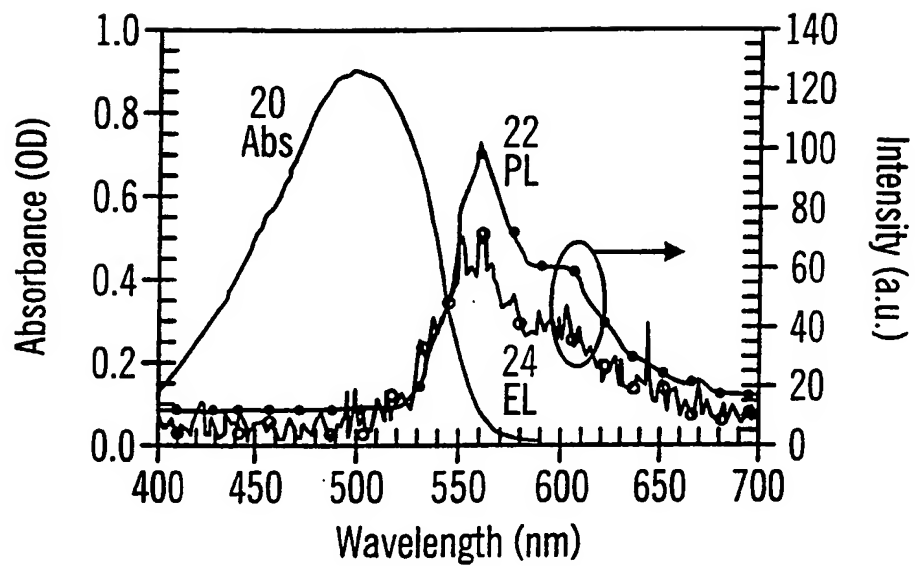


FIG. 2

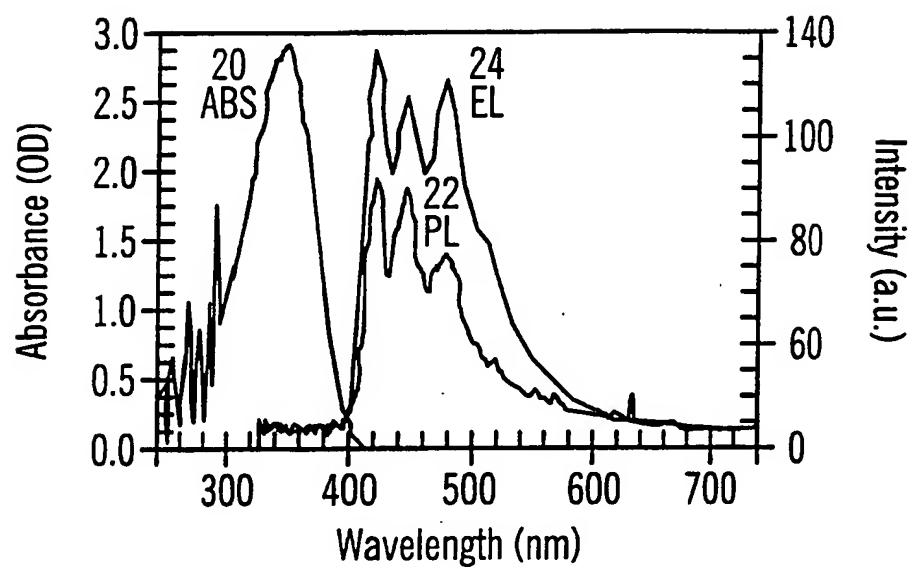


FIG. 3

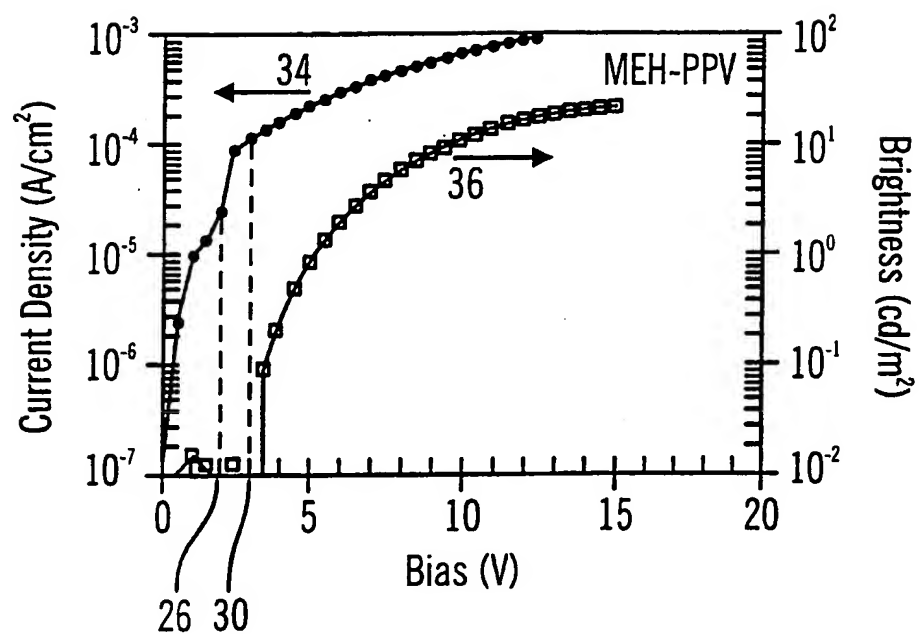


FIG. 4

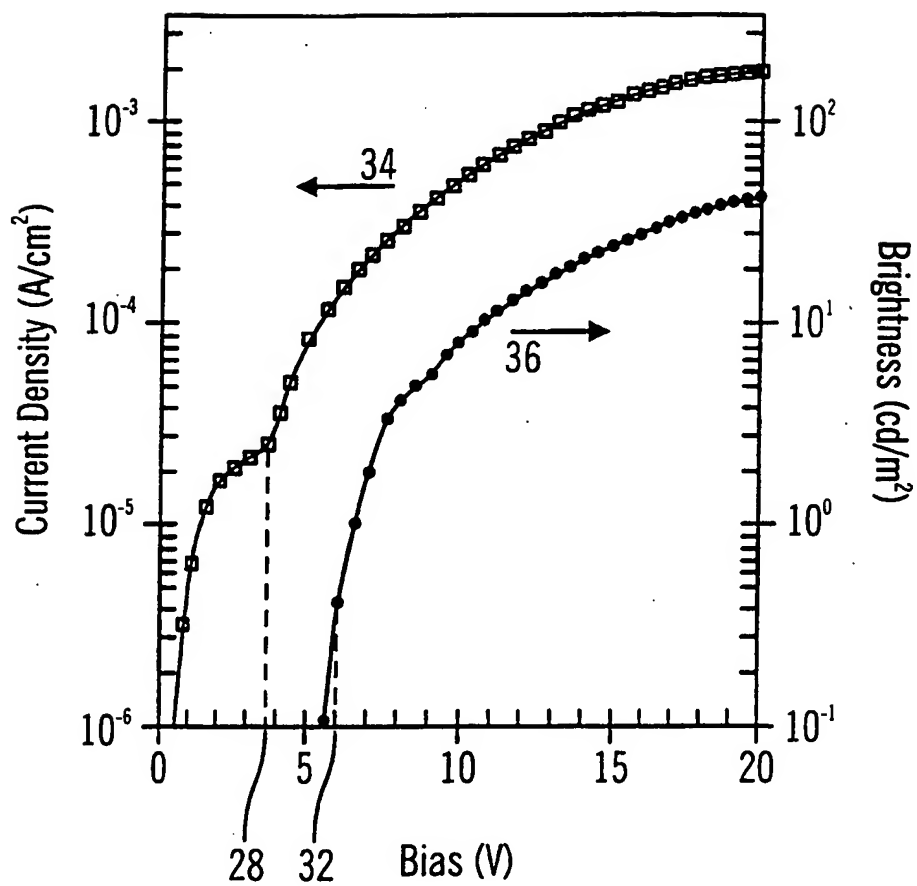


FIG. 5

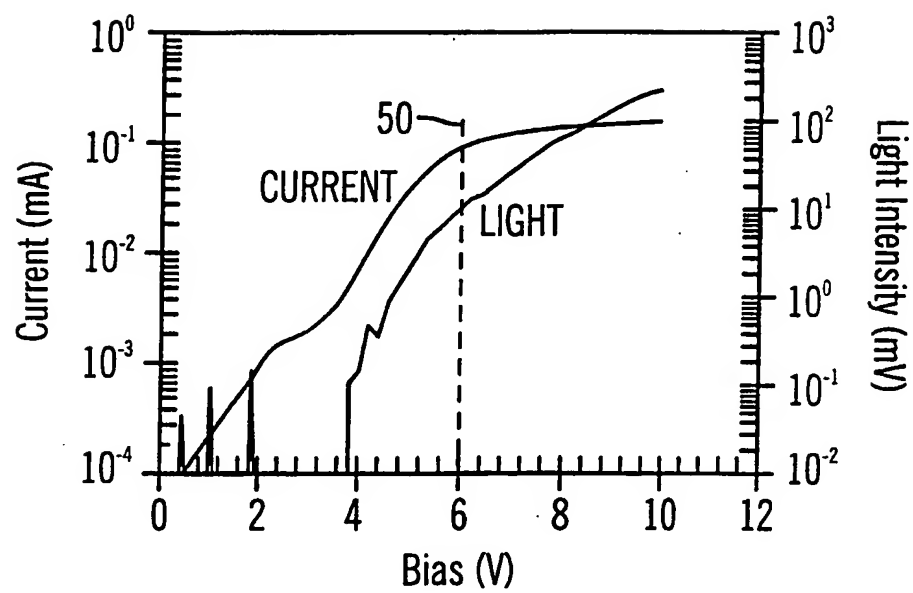


FIG. 6

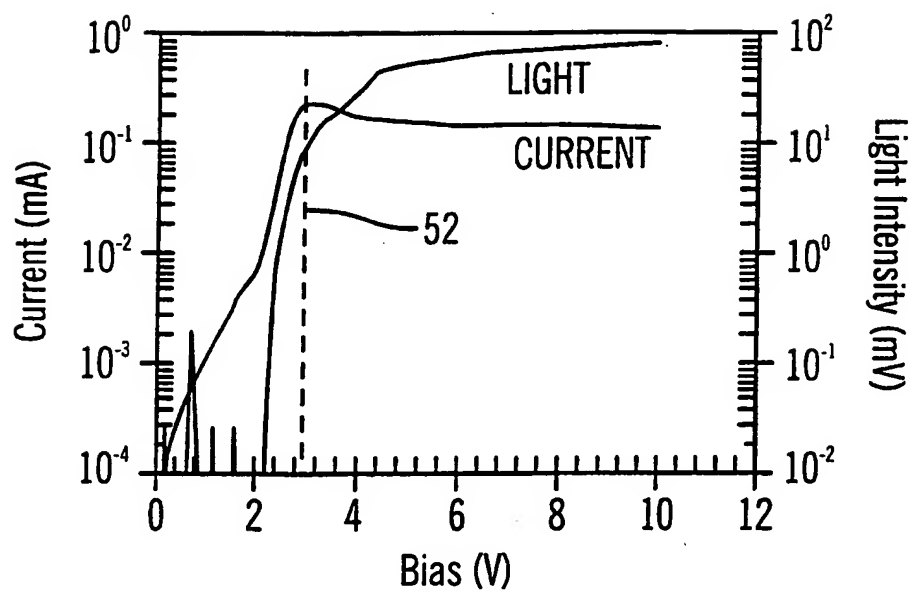


FIG. 7

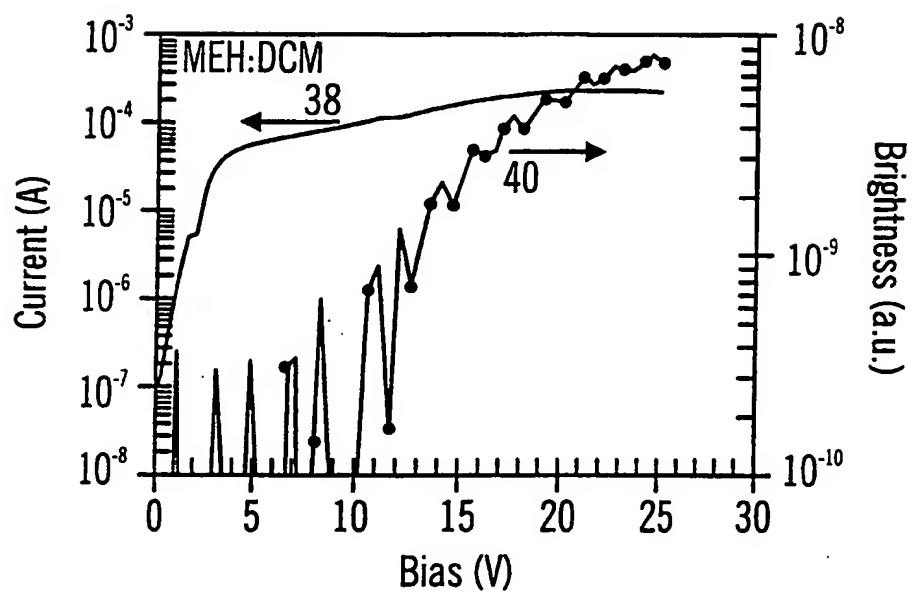


FIG. 8

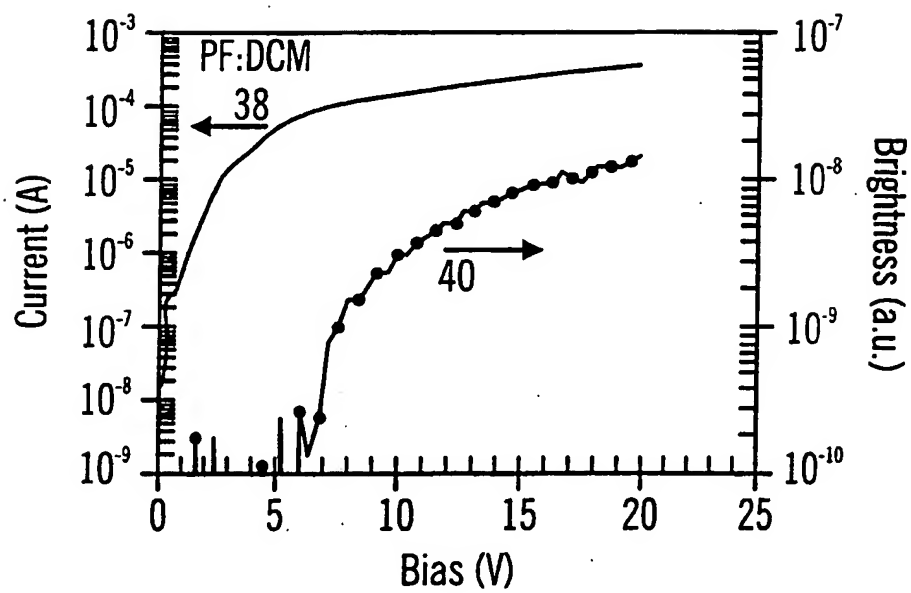


FIG. 9

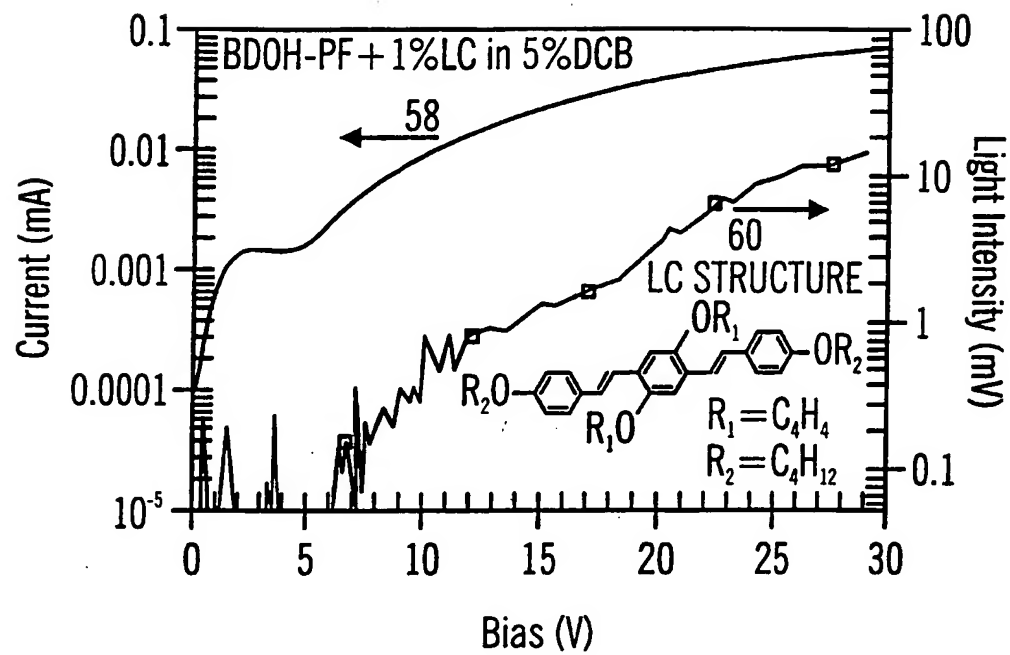


FIG. 10

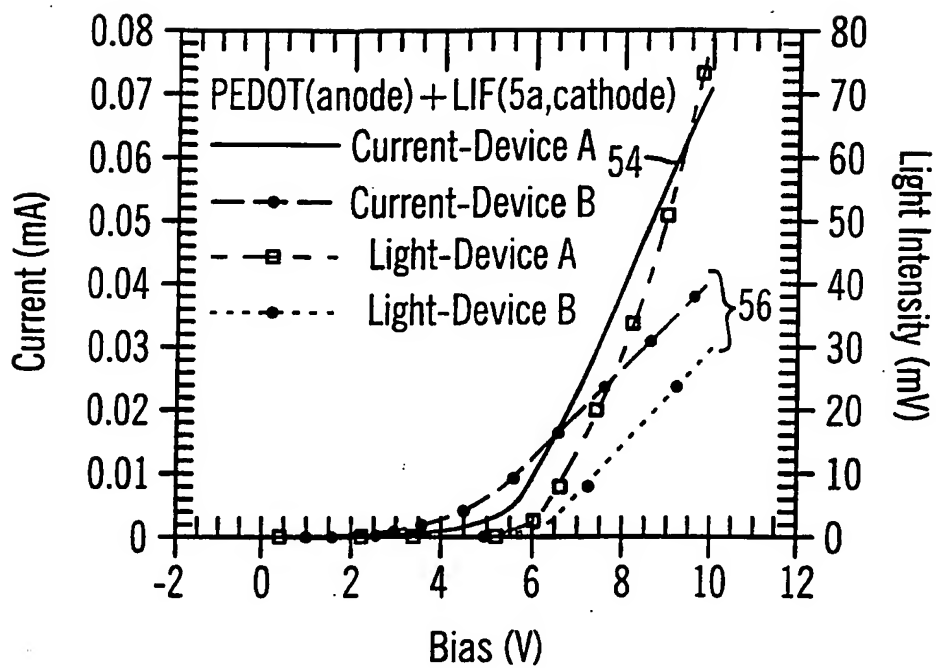


FIG. 11

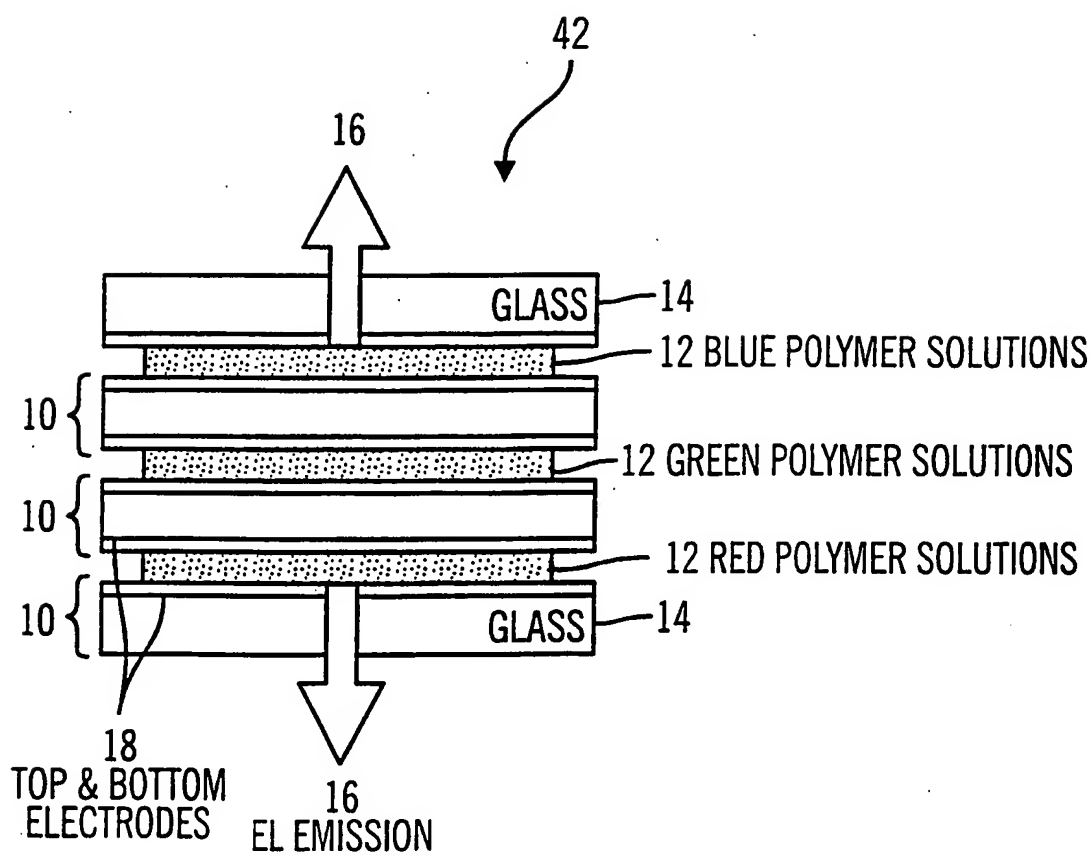


FIG. 12

Multicolor display made of SLEDs

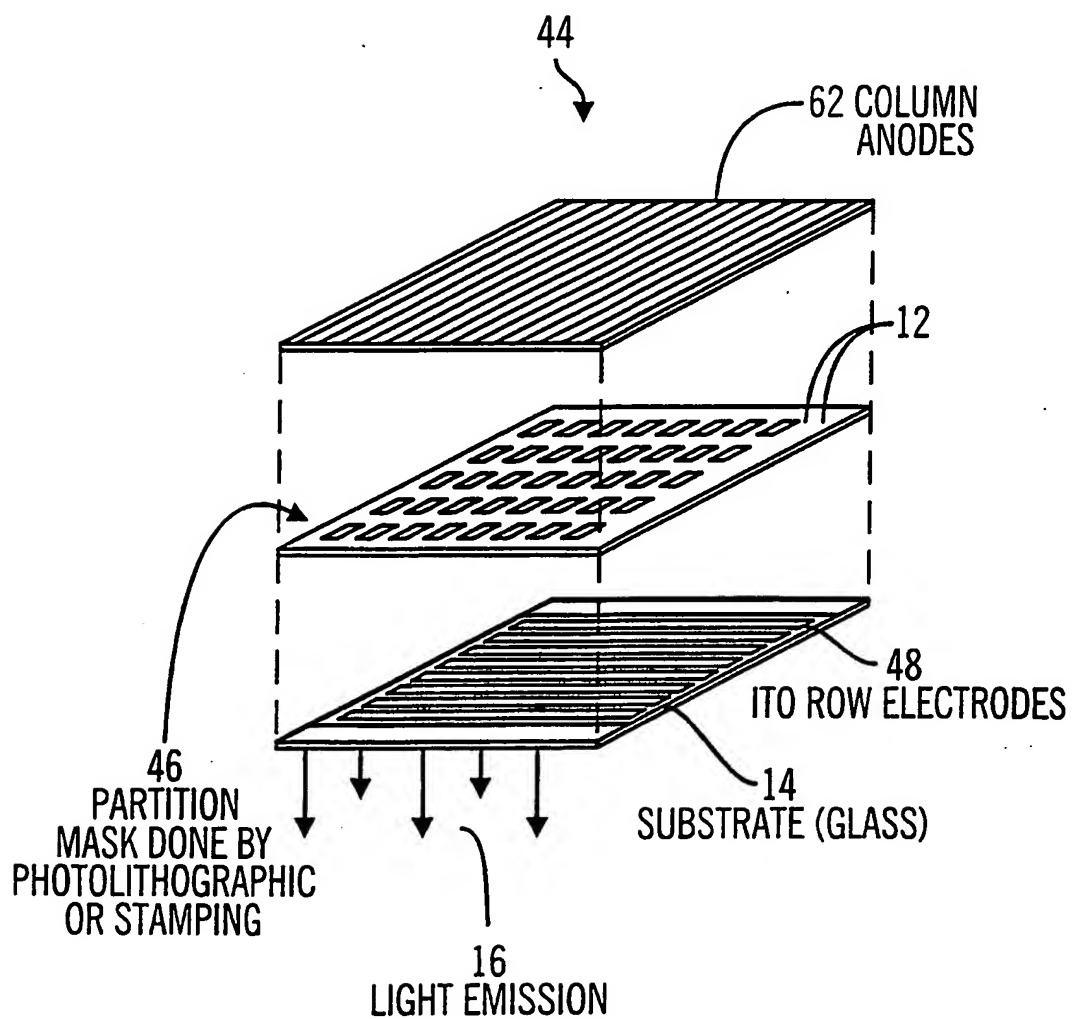


FIG. 13

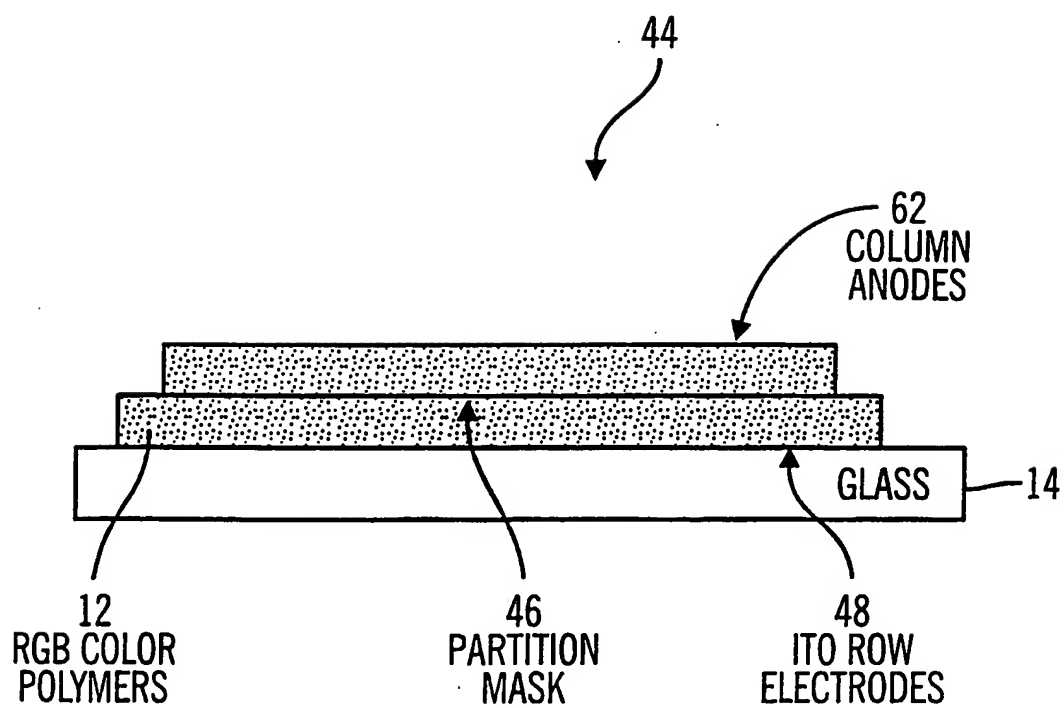


FIG. 14

INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 99/27024

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 F21K2/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H05B H01L F21K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YANG Y ET AL: "EFFICIENT BLUE-GREEN AND WHITE LIGHT-EMITTING ELECTROCHEMICAL CELLSBASED ON POLYU9,9-BIS(3,6-DIOXAHEPTYL)-FLUORENE-2,7-DIYL" JOURNAL OF APPLIED PHYSICS,US,AMERICAN INSTITUTE OF PHYSICS. NEW YORK, vol. 81, no. 7, 1 April 1997 (1997-04-01), pages 3294-3298, XP000658514 ISSN: 0021-8979 the whole document	1,2,4, 12,15,21
A	WO 96 00983 A (UNIX CORP) 11 January 1996 (1996-01-11) the whole document	1-3,8, 12,15,21
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

Date of the actual completion of the international search

2 March 2000

Date of mailing of the international search report

17/03/2000

Name and mailing address of the ISA

European Patent Office, P.B. 6818 Patentaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx 31 631 epo nl,
Fax: (+31-70) 340-3018

Authorized officer

De Laere, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/27024

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HAMAGUCHI M ET AL: "A COMPARATIVE STUDY OF D-C ELECTROCHEMILUMINESCENCE FROM POLY(2-METHOXY-5-DODECYLOXY-P-PHENYLENEVINYLENE) IN SOLUTION AND IN SOLID POLYMER ELECTROLYTE MEDIA" JAPANESE JOURNAL OF APPLIED PHYSICS, JP, PUBLICATION OFFICE JAPANESE JOURNAL OF APPLIED PHYSICS. TOKYO, vol. 36, no. 6A, PART 02, 1 June 1997 (1997-06-01), pages L679-L681, XP000727773 ISSN: 0021-4922	1-3,21
A	KOGO K ET AL: "POLARIZED LIGHT EMISSION FROM A CALAMITIC LIQUID CRYSTALLINE SEMICONDUCTOR DOPED WITH DYES" APPLIED PHYSICS LETTERS, US, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, vol. 73, no. 11, 14 September 1998 (1998-09-14), pages 1595-1597, XP000784080 ISSN: 0003-6951 the whole document	1,2,12,15,21
A	SCHAPER H ET AL: "New aspect of D-C electrochemiluminescence" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, JUNE 1982, USA, vol. 129, no. 6, pages 1289-1294, XP002132031 ISSN: 0013-4651 the whole document	1,15,21

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 99/27024

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9600983 A	11-01-1996	US 5682043 A	28-10-1997
		AU 2911995 A	25-01-1996
		EP 0767974 A	16-04-1997
		JP 10506747 T	30-06-1998